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(54) **COMPOSITIONS THAT CAN PRODUCE POLYMERS**

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(57) **ABSTRACT**

This invention provides a compositions that are useful for polymerizing at least one monomer into at least one polymer.

39 Claims, No Drawings

TABLE X-continued

Ex. #	A[1]	Treatment	S[2]	Metallocene[6]	P[3]	T[4]	A[5]
69	Alumina	F/Cl 600C	0.0213	C	15.8	64.2	693
70	Alumina	F/Cl 600C	0.1000	D	83.9	61.5	819

Table-IX Notes
[1]This is the solid oxide compound used.
[2]This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
[3]This is the amount of polymer produced in grams.
[4]This is the amount of time used in minutes.
[5]This is the activity in gP/(gS · hr).
[6]A = bis(n-butylcyclopentadienyl) zirconium dichloride
B = bis(cyclopentadienyl) zirconium dichloride
C = bis(cyclopentadienyl) hafnium dichloride
D = bis(n-butylcyclopentadienyl) zirconium chloride trimethylsilysmethyl

TABLE IX

Ex. #	A[1]	Treatment	S[2]	CC[3]	P[4]	T[5]	A[6]
56[7]	Alumina	Chlorided	0.1866	AlEt3	336.0	60.0	1800
57	Alumina	Chlorided	0.1958	GaMe3	0	60.0	0
58	Alumina	Chlorided	0.1878	ZnEt2	0	60.0	0
59	Alumina	Chlorided	0.1756	MgBu2	2.5	60.0	14
60	Alumina	Chlorided	0.1966	AlEt2H	52.6	60.0	268
61	Alumina	Chlorided	0.1777	Al(I-Bu)3	293	60.0	1649
62	Alumina	Chlorided	0.1840	LiHex	0	60.0	0
63	Alumina	Fluorided	0.2253	AlEt3	281.6	60.0	1250
64	Alumina	Fluorided	0.2181	AlMe3	154.2	60.0	707
65	Alumina	Fluorided	0.2307	AlEt2Cl	0	40.0	0
66	Alumina	Fluorided	0.2465	BEt3	0	30.0	0

Table-IX Notes
[1]This is the solid oxide compound used.
[2]This is the amount of solid oxide compound, in grams, being contacted with the other compounds.
[3]This is the amount, in milliliters, of cocatalyst used.
[4]This is the amount of polymer produced in grams.
[5]This is the amount of time used in minutes.
[6]This is the activity in gP/(gS · hr).
[7]The amount of organometal compound used was 25 micromoles. The type of organometal compound used was bis(n-butylcyclopentadienyl) zirconium dichloride. This organometal compound was in a solution that contained 0.5 grams of bis(n-butylcyclopentadienyl) zirconium dichloride per 100 milliliters of toluene. Additionally, these example were run at 90° C., under 550 psig ethylene, in 1.2 liters of isobutane.

That which is claimed is:

1. A process to produce a composition of matter, said process comprising contacting at least one organometal compound, at least one treated solid oxide compound, and at least one organoaluminum compound to produce said composition,

wherein said organometal compound has the following general formula

$(X^1)(X^2)(X^3)(X^4)M^1$

wherein M^1 is selected from the group consisting of titanium, zirconium, and hafnium, and

wherein (X^1) is independently selected from the group consisting of cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, and

wherein said substituents on said substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, are selected from the group consisting of aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and hydrogen; and

wherein (X^3) and (X^4) are independently selected from the group consisting of halides, aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and

wherein (X^2) is selected from the group consisting of Group OMC-I or Group OMC-II,

wherein said organoaluminum compound has the following general formula,

$Al(X^5)_n(X^6)_{3-n}$

wherein (X^5) is a hydrocarbyl having from 1–20 carbon atoms, and

wherein (X^6) is a halide, hydride, or alkoxide, and wherein "n" is a number from 1 to 3 inclusive,

wherein said treated solid oxide compound is produced by a process comprising contacting at least one solid oxide compound with an electron-withdrawing anion source compound; and

wherein said at least one solid oxide compound is calcined before, during or after contacting said electron-withdrawing anion source;

wherein the activity of said composition is greater than 250 grams of polyethylene per gram of treated solid oxide compound per hour; and

wherein there is a substantial absence of aluminoxanes and organoborates.

2. A process to produce a composition of matter, said process comprising contacting at least one organometal compound, at least one treated solid oxide compound, and at least one organoaluminum compound to produce said composition,

wherein said composition can polymerize ethylene into a polymer with an activity greater than 250 (gP/(gS·hr)), and

wherein said organometal compound has the following general formula

$(X^1)(X^2)(X^3)(X^4)M^1$

wherein M^1 is selected from the group consisting of titanium, zirconium, and hafnium, and

wherein (X^1) is independently selected from the group consisting of cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, and

wherein said substituents on said substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, are selected from the group consisting of aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and hydrogen; and

wherein (X^3) and (X^4) are independently selected from the group consisting of halides, aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and

wherein (X^2) is selected from the group consisting of Group OMC-I or Group OMC-II,

wherein said organoaluminum compound has the following general formula,

$$Al(X^5)_n(X^6)_{3-n}$$

wherein (X^5) is a hydrocarbyl having from 1–20 carbon atoms, and

wherein (X^6) is a halide, hydride, or alkoxide, and

wherein "n" is a number from 1 to 3 inclusive, and

wherein said treated solid oxide compounds comprise oxygen and at least one element selected from the group consisting of groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 of the periodic table, including lanthanides and actinides,

wherein said treated solid oxide compound is produced by a process comprising contacting at least one solid oxide compound with an electron-withdrawing anion source compound; and

wherein said at least one solid oxide compound is calcined before, during or after contacting said electron-withdrawing anion source; and

wherein there is a substantial absence of aluminoxanes and organoborates in said composition.

3. A process according to claim 2 wherein said activity is greater than 250.

4. A process according to claim 3 wherein said activity is greater than 500.

5. A process according to claim 4 wherein said activity is greater than 1000.

6. A process according to claim 5 wherein said activity is greater than 2000.

7. A composition produced by the process of claim 2.

8. A process according to claim 2

wherein said composition can polymerize ethylene into a polymer with an activity greater than 2000 (gP/(gS·hr)), and

wherein said organometal compound is selected from the group consisting of

bis(cyclopentadienyl)hafnium dichloride;

bis(cyclopentadienyl)zirconium dichloride;

(ethyl(indenyl)$_2$)hafnium dichloride;

(ethyl(indenyl)$_2$)zirconium dichloride;

(ethyl(tetrahydroindenyl)$_2$)hafnium dichloride;

(ethyl(tetrahydroindenyl)$_2$)zirconium dichloride;

bis(n-butylcyclopentadienyl)hafnium dichloride;

bis(n-butylcyclopentadienyl)zirconium dichloride;

((dimethyl)(diindenyl)silane)zirconium dichloride;

((dimethyl)(diindenyl)silane)hafnium dichloride;

((dimethyl)(ditetrahydroindenyl)silane)zirconium dichloride;

((dimethyl)(di(2-methyl indenyl))silane)zirconium dichloride;

bis(fluorenyl)zirconium dichloride, and

wherein said organoaluminum compound is selected from the group consisting of

trimethylaluminum;

triethylaluminum;

tripropylaluminum;

diethylaluminum ethoxide;

tributylaluminum;

triisobutylaluminum hydride;

triisobutylaluminum;

diethylaluminum chloride, and

wherein said solid oxide compound is selected from the group consisting of Al_2O_3, B_2O_3, BcO, Bi_2O_3, CdO, Co_3O_4, Cr_2O_3, CuO, Fe_2O_3, Ga_2O_3, La_2O_3, Mn_2O_3, MoO_3, NiO, P_2O_5, Sb_2O_5, SiO_2, SnO_2, SrO, ThO_2, TiO_2, V_2O_5, WO_3, Y_2O_3, ZnO, ZrO_2; and mixtures thereof, and

wherein said treated solid oxide compound has been contacted with fluoride or chloride or both.

9. A process according to claim 1 consisting essentially of contacting said organometal compound, said treated solid oxide compound, and said organoaluminum compound to produce said composition.

10. A process according to claim 2 consisting essentially of contacting said organometal compound, said treated solid oxide compound, and said organoaluminum compound to produce said composition.

11. A process according to claim 2 wherein said treated solid oxide compound is produced by a process comprising:

1) contacting a solid oxide compound with at least one electron-withdrawing anion source compound to form a first mixture; and

2) calcining said first mixture to form said treated solid oxide compound.

12. A process according to claim 11 wherein said electron-withdrawing anion source compound is selected from the group consisting of sulfates, halides, and triflate.

13. A process according to claim 12 wherein said calcining is conducted for about 1 hour to about 10 hours at a temperature in the range of about 400 to about 800° C.

14. A process according to claim 1 wherein said treated solid oxide compound is produced by a process comprising:

1) contacting at least one solid oxide compound with a first electron-withdrawing anion source compound to form a first mixture;

2) calcining said first mixture to produce a calcined first mixture;

3) contacting said calcined first mixture with a second electron-withdrawing anion source compound to form a second mixture; and

4) calcining said second mixture to form said treated solid oxide compound.

15. A process according to claim 2 wherein said composition is produced by a process comprising:

1) contacting said organometal compound and said treated solid oxide compound together for about 1 minute to about 1 hour at a temperature of about 25 to about 100° C. to form a first mixture,

2) contacting said first mixture with an organoaluminum compound to form the composition.

16. A process to produce a composition, said process comprising:

1) calcining alumina for 3 hours at 600° C. to produce a calcined alumina;

2) contacting said calcined alumina with carbon tetrachloride to produce a chlorided alumina;

3) combining said chlorided alumina with bis(n-buytlcyclopentadienyl)zirconium dichloride for 1 minute to 1 hour at a temperature in a range of about 25 to about 100° C. to produce a mixture; and

4) combining said mixture and triethylaluminum to produce said composition.

17. A composition produced by the process of claim 1.

18. A composition produced by the process of claim 9.

19. A composition produced by the process of claim 10.

20. A composition produced by the process of claim 16.

21. A composition according to claim 7 wherein said composition subsequent to contacting the organometal compound, treated solid oxide compound, and organoaluminum compound consists essentially of organometal compound and treated solid oxide compound.

22. A composition according to claim 21 wherein said composition subsequent to contacting the organometal compound, treated solid oxide compound, and organoaluminum compound consists essentially of organometal compound, treated solid oxide compound, and organoaluminum compound.

23. A process comprising:

1) contacting an oxide selected from alumina, silica-alumina, aluminophosphate, and mixtures thereof with at least one treating agent selected from sulfating agents, fluoriding agents, and chloriding agents to produce a treated oxide;

2) calcining said treated oxide to produce a calcined treated oxide; and

3) combining (1) said treated oxide, (2) an organoaluminum compound selected from triethylaluminum, triisobutylaluminum, and mixtures thereof; and (3) an organometal compound.

24. A process according to claim 23 wherein said organometal compound is bis(n-butylcyclopentadienyl) zirconium dichloride.

25. A process according to claim 23 wherein said treating agent is a fluoriding agent and a chloriding agent.

26. A process according to claim 25 wherein said fluoriding agent and chloriding agent are contacted sequentially with said oxide.

27. A process according to claim 26 wherein said fluoriding agent is perfluorohexane and said chloriding agent is carbon tetrachloride.

28. A process according to claim 23 wherein said oxide is calcined before said contacting and calcined after said contacting.

29. A process according to claim 23 wherein said oxide is calcined during said contacting.

30. A process according to claim 23 wherein said contacting is carried out by impregnation and the resulting impregnated oxide is dried before said calcining.

31. A process according to claim 23 wherein said treating agent is ammonium sulfate.

32. A process according to claim 23 wherein said treating agent is trifluoromethane and sulfonic acid.

33. A process according to claim 23 wherein said treating agent is selected from sulfuric acid and ammonium sulfate.

34. A process according to claim 23 wherein said treating agent is ammonium bifluoride.

35. A process according to claim 23 wherein said treating agent is selected from thionyl chloride and sulfuryl chloride.

36. A catalyst composition produced by the process of claim 23.

37. A catalyst composition produced by the process of claim 25.

38. A process to produce a composition of matter, said process consisting essentially of contacting at least one organometal compound, at least one treated solid oxide compound, and at least one organoaluminum compound to produce said composition,

wherein said organometal compound has the following general formula

$$(X^1)(X^2)(X^3)(X^4)M^1$$

wherein M^1 is selected from the group consisting of titanium, zirconium, and hafnium, and

wherein (X^1) is independently selected from the group consisting of cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, and

wherein said substituents on said substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, are selected from the group consisting of aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and hydrogen; and

wherein (X^3) and (X^4) are independently selected from the group consisting of halides, aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and

wherein (X^2) is selected from the group consisting of Group OMC-I or Group OMC-II,

wherein said organoaluminum compound has the following general formula,

$$Al(X^5)_n(X^6)_{3-n}$$

wherein (X^5) is a hydrocarbyl having from 1–20 carbon atoms, and

wherein (X^6) is a halide, hydride, or alkoxide, and

wherein "n" is a number from 1 to 3 inclusive,

wherein said treated solid oxide compound is produced by a process comprising contacting at least one solid oxide compound with an electron-withdrawing anion source compound; and

wherein said at least one solid oxide compound is calcined before, during or after contacting said electron-withdrawing anion source;

wherein the activity of said composition is greater than 250 grams of polyethylene per gram of treated solid oxide compound per hour;

wherein there is a substantial absence of aluminoxanes and organoborates.

39. A process to produce a composition of matter, said process consisting essentially of contacting at least one organometal compound, at least one treated solid oxide compound, and at least one organoaluminum compound to produce said composition,

wherein said composition can polymerize ethylene into a polymer with an activity greater than 250 (gP/(gS·hr)), and

wherein said organometal compound has the following general formula

$$(X^1)(X^2)(X^3)(X^4)M^1$$

wherein M^1 is selected from the group consisting of titanium, zirconium, and hafnium, and

wherein (X^1) is independently selected from the group consisting of cyclopentadienyls, indenyls, fluorenyls, substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, and

wherein said substituents on said substituted cyclopentadienyls, substituted indenyls, and substituted fluorenyls, are selected from the group consisting of aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and hydrogen; and

wherein (X^3) and (X^4) are independently selected from the group consisting of halides, aliphatic groups, cyclic groups, combinations of aliphatic and cyclic groups, and organometallic groups, and

wherein (X^2) is selected from the group consisting of Group OMC-I or Group OMC-II,

wherein said organoaluminum compound has the following general formula,

$$Al(X^5)_n(X^6)_{3-n}$$

wherein (X^5) is a hydrocarbyl having from 1–20 carbon atoms, and

wherein (X^6) is a halide, hydride, or alkoxide, and

wherein "n" is a number from 1 to 3 inclusive, and

wherein said treated solid oxide compounds comprise oxygen and at least one element selected from the group consisting of groups 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 of the periodic table, including lanthanides and actinides,

wherein said treated solid oxide compound is produced by a process comprising contacting at least one solid oxide compound with an electron-withdrawing anion source compound; and

wherein said at least one solid oxide compound is calcined before, during or after contacting said electron-withdrawing anion source; and

wherein there is a substantial absence of aluminoxanes and organoborates in said composition.

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